Local off-cubic distortion the cause for the low- and high-spin states of the Co^{3+} ion*

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It is pointed out that it is the local symmetry that determines the realization of the low- and high-spin state of the Co^{3+} ion. We can rigorously prove it treating the Co^{3+} ion as the highly-correlated electron system $3d^6$, that fulfiles the Hund's rules with taking into account the spin-orbit coupling. As the function of the sign of the off-cubic crystal-field distortion the magnetic or non-magnetic state is realized.

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The origin of low- and high-spin states of the Co^{3+} ion formed in different ionic compounds is under the long debate in the 3d magnetism.[1−6] A non-magnetic state observed in $LaCoO_3$, for instance, is very intriguing having in mind the strong magnetic Co state realized in CoO that is antiferromagnet with T_N of 289 K. An argument that the cobalt ion in the high oxidation state (Co^{3+}) likes to be in the low-spin state does not hold as $SrCoO_{2.5}$, where also the trivalent cobalt ion exists, shows extremely strong antiferromagnetic state (T_N of 570 K). Following Van Vleck the realization of the low- or high-spin state is often discussed in the one-electron model as resulting from the delicate interplay of the crystal-field and intra-atomic exchange (Hund coupling) energies (see e.g. Ref. 5). Despite of the numerous very different versions of the one-electron description (LDA, LSDA, ... +GGA, ...) this approach still has serious difficulty in the satisfactory systematic description of e.g. the $LaMO_3$ (M=Ti-Cu) series. It produces e.g. often wrongly the metallic state instead of the insulating/semiconducting state.[2]

The aim of this Letter is to point out that it is the local symmetry that determines the realization of the low- or high-spin state of the Co^{3+} ion. We can prove it for the Co^{3+} ion placed at the slightly distorted octahedral site. It turns out that in the CoO_6 octahedra the Co^{3+} ion at the absolute zero temperature can have the magnetic moment as large as 3.6 μ_B or null as the function of the sign of the local off-cubic distortion. In case of the rhombohedral distortion the change of the sign is associated with the compression or the elongation of the octaedron along the main cube diagonal. The same strong dependence of the atomic magnetic moment holds for the tetragonal distortion.

We treat the Co^{3+} ion in a solid as the highly-correlated electron system $3d^6$ with 6 electrons in the unfilled 3d shell. These high correlations assure the realization of Hund's rules. We have calculated the energy spectrum of such the system for the ground state described by the Hund's rules quantum numbers S=2 and L=2 taking into account the spin-orbit (s-o) coupling. We have taken the spin-orbit coupling rigorously into account, not by approximate perturbation methods as is usually made in the current literature, if the s-o coupling is considered at all. This 25-level discrete energy spectrum depends on the detailed shape of the electric-field potential formed by local charge surroundings. This detailed shape of the electric potential can be represented by means of the multipolar expansion of spherical harmonics. These multipolar charge interactions in the CoO_6 octahedra can be accounted for by consideration of the crystal-field Hamiltonian[7]

$H_{CF} = B_4^d(O_4^0 - 20\sqrt{2}O_4^3) + B_2^0 O_2^0$.

The first term accounts for the multipolar charge interactions of the cubic symmetry with z axis taken along the main diagonal. The second term accounts for the simplest off-cubic distortion and $O_2^0 = 3L_z^2 - L(L+1)$. The cubic term in combination with the s-o coupling, $\lambda_{s-o}\ L \cdot S$, yields[8] 3-fold degenerated ground state in the $|LSL_zS_z\rangle$ space with the corresponding magnetic moments of 0 (singlet) and $\pm 3.5\ \mu_B$ (doublet). The off-cubic distortion splits these states making the ground state magnetic (doublet) or non-magnetic (the singlet) as the function of the sign of the B_2^0 parameter. The change of the sign of B_2^0 can be realized by the compression or the elongation of the octaedron along the main cube diagonal in the case of the rhombohedral distortion. The magnetic doublet forms the long-range magnetic state in contrast to the singlet state that yields the diamagnetic behaviour like it is in $LaCoO_3$, for instance. These calculations have been performed with the realistic values: B_4^d= -11.5 meV and the spin-orbit coupling λ_{s-o} of

-18 meV. $B_2^0 > 0$ yields the non-magnetic ground state [9]. B_2^0 of e.g. 2 meV produces the spin-like gap of 1.9 meV with the highly-magnetic excited doublet with the moment of 3.0 μ_B. Such the electronic structure has been recently suggested to exist in $LaCoO_3$ by Zhuang et al.[6] (m=2.9 μ_B).

In conclusion, we argue that the formation of the non-magnetic or the magnetic state of the Co^{3+}-ion containing compounds, discussed in the current literature as the Co^{3+} low- and high-spin states, results from the sign of the local off-cubic crystalline-electric-field distortion. It can be exactly calculated treating the Co^{3+} ion as the highly-correlated $3d^6$ system that experiences the cubic crystal-field interactions provided the spin-orbit coupling is correctly taken into account. The proposed mechanism, the strong correlation of the local magnetic moment and the detailed shape of the crystal-field potential experienced by the paramagnetic ion, is known to work well for rare-earth ion compounds [10-12] but has not been used so far for $LaCoO_3$. We would like to notice that the obtained correlation of the local magnetic moment and the local symmetry is very general. In particular, it does not depend on the used parameters provided the sign of three parameters B_4^d, B_2^0 and the spin-orbit coupling λ_{s-o} is preserved. Moreover, the proposed single-ion-like crystal-field-based model yields in the natural way the insulating state experimentally-observed for most of 3d-ion compounds like in $LaCoO_3$.

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